Whole Air Sampling during NASA's March-April 1999 Pacific Exploratory Expedition (PEM-Tropics B)

End of Project Report
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Donald R. Blake
Department of Chemistry
University of California, Irvine

University of California, Irvine (UCI) collected more than 4500 samples whole air samples collected over the remote Pacific Ocean during NASA's Global Tropospheric Experiment (GTE) Pacific Exploratory Mission-Tropics B (PEM-Tropics B) in March and early April 1999. Approximately 140 samples during a typical 8-hour DC-8 flight, and 120 canisters for each 8-hour flight aboard the P-3B. These samples were obtained roughly every 3-7 min during horizontal flight legs and 1-3 min during vertical legs. The filled canisters were analyzed in the laboratory at UCI within ten days of collection. The mixing ratios of 58 trace gases comprising hydrocarbons, halocarbons, alkyl nitrates and DMS (see Table 1) were reported (and archived) for each sample. Two identical analytical systems sharing the same standards were operated simultaneously around the clock to improve canister turn-around time and to keep our measurement precision optimal [*Sive,* 1998; *Colman, 2001*, *Simpson et al.*, 2000].

A summary of our results for samples collected over remote regions of the Pacific are presented in Table 2. Compared to the late August-early October 1996 PEM-Tropics A experiment, the large-scale spatial PEM-Tropics B distributions of NMHCs and C_2Cl_4 revealed a much more pronounced north-south inter-hemispheric gradient, with higher concentrations in the north and lower levels in the south [*Blake et al.*, 2001a]. Strong continental outflow and winter-long accumulation of pollutants led to seasonally high Northern Hemisphere trace gas levels during PEM-Tropics B. Penetration of air exhibiting aged northern hemisphere characteristics was frequently observed at low altitudes over the equatorial central and western Pacific south to about 5°S.

The different air masses observed over the North Pacific frequently were associated with distinct source regions and photochemical conditions. Flow from the

west brought air containing mixing ratios of trace gases that were significantly higher than reported for PEM-Tropics A. These pollution levels were most elevated below about 5 km, and many ten-day backward trajectories originated over the Asian continent. Above about 1 km these air masses contained chemical signatures characteristic of biomass burning and emissions of Halon 1211 associated with developing nations. These backward trajectories typically originated over Southern Asian regions. By contrast, air at the lowest altitudes often originated from higher northern latitudes and had characteristics of emissions from developed nations such as Japan, Northern Europe, and North America.

The spatial distributions of light alkyl nitrates were remarkably similar for both the September-October 1996 PEM-Tropics A and March-April 1999 PEM-Tropics B, accounting for a large fraction of NO_y in the equatorial MBL [*Blake et al.*, 2001b]. These consistently high equatorial mixing ratios provide the strongest evidence yet to establish the ocean as the major source for $MeONO_2$. Further, these results support the suggestion that CH_3I, $CHBr_3$, and DMS emissions are not necessarily coupled to the emission of biogenically produced C_1-C_3 alkyl nitrates. In *Blake et al.*, 2001b, we suggest a link between our equatorial findings and the enhanced $MeONO_2$ concentrations observed previously over the other major area of high nutrient-low chlorophyll waters, such as the Southern Ocean around Antarctica. Integrating these observations with HNLC regions, as defined by satellite measurements of chlorophyll and oceanic nitrate analysis, may assist calculations that better assess the large-scale influence of ocean-source alkyl nitrates on the remote atmosphere.

Ethyl nitrate has a dominant oceanic source in equatorial regions, but at mid NH latitudes a small additional source is associated with urban/industrial emissions. The low altitude distribution of 2-$PrONO_2$ appears to be almost equally influenced by equatorial oceanic and by anthropogenic NH emissions. Similar equatorial MBL mixing ratios were observed for both PEM-Tropics A and B, so no seasonal factors (which are minimal at the equator) were apparent. The stable oceanic emission factors may make a useful diagnostic for air masses that have recently been at low altitude over the equatorial Pacific Ocean, compared to the much lower $MeONO_2$:$EtONO_2$ ratios typically observed in air masses which have been influenced by urban/industrial emissions. The high 2-

$PrONO_2$:$MeONO_2$ and 2-$BuONO_2$:$MeONO_2$ ratios for the corresponding anthropogenic-influenced NH air masses also provide a useful air mass characterization signature.

The relative lack of southern hemisphere biomass burning sources and the westerly position of the South Pacific convergence zone contributed to significantly lower PEM-Tropics B mixing ratios of the NMHCs and CH_3Cl south of 10°S compared to PEM-Tropics A. Therefore, the trace gas composition of the South Pacific troposphere was considerably more representative of minimally polluted tropospheric conditions during PEM-Tropics B.

References

Blake, N. J., D. R. Blake, I. J. Simpson, J. P. Lopez, N. A. Ciszkowski, A. L. Swanson, A. S. Katzenstein, S. Meinardi, B. C. Sive, J. J. Colman, E. Atlas, F. Flocke, S. A. Vay, M. A. Avery, and F. S. Rowland, Large scale latitudinal and vertical distributions of NMHCs and selected halocarbons in the troposphere over the Pacific Ocean during the March-April 1999 Pacific Exploratory Expedition (PEM-Tropics B), *J. Geophys. Res.*, in press (Ist Special Issue), 2001.

Blake, N. J., D. R. Blake, A. L. Swanson, E. Atlas, F. Flocke, and F. S. Rowland, Latitudinal, vertical, and seasonal variations of C_1-C_4 alkyl nitrates in the troposphere over the Pacific Ocean during PEM-Tropics A and B: Oceanic and continental sources, *J. Geophys. Res.*, in preparation for second Special Issue, 2001b.

Coleman, J. J., A. L. Swanson, S. Meinarde, and D. R. Blake, Description of the analysis of a wide range of volatile organic compounds in whole air samples collected during PEM-Tropics A and B, *Anal. Chem., 73,* 3723-3731, 2001.

Simpson, I. J., J. J. Colman, A. L. Swanson, A. R. Bandy, D. C. Thornton, D. R. Blake, and F. S. Rowland, Aircraft measurements of dimethyl sulfide (DMS) using a whole air sampling technique, submitted to *J. Atmos. Chem,* 2000.

Sive, B. C., Atmospheric NMHCs: Analytical methods and estimated hydroxyl radical concentrations, Ph.D. Thesis, University of California, Irvine, 1998.

Table 1. Gases reported (and archived) by the UC Irvine lab during PEM-Tropics B

HCFC-134a	CH2Br2	1-Butene
HCFC-22	CHBr3	i-butene
HCFC-142b	CH2BrCl	c-2-butene
HCFC-141B	CHBr2Cl	i-Pentane
CFC-12	CHBrCl2	n-Pentane
CFC-11	CH3ONO2	Isoprene
CFC-113	C2H5ONO2	n-hexane
CFC-114	i-C3H7ONO2	Cyclo-hexane
CH3Cl	n-C3H7ONO2	Benzene
CH3Br	2-C4H9ONO2	n-heptane
CH2Cl2	Ethane	Toluene
CHCl3	Ethylene	n-octane
CH3CCl3	Ethyne	Ethyl-benzene
CCl4	Propene	m/p-xylene
1-2-C2H4Cl2	Propane	p/m-xylene
C2Cl4	Cyclo-propane	o-xylene
H-1211	i-Butane	2-2-4-trimethylpentane
H-2402	Propa-diene	2-3-4-trimethylpentane
DMS	n-Butane	
CH3I	t-2-butene	